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pH METERS
[pH-Wert-Messtechnik]

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Precise, electrometric measurement of pH and other ion activities is greatly simplified for practical applications by means of a sophisticated physical and chemical solution with the entire measuring setup permanently stabilized. The electrolyte for the reference electrode and the activating solution for the measuring electrode are usually identical in this new rapid-measurement concept. This completely eliminates various measuring errors often neglected in practice as well as the frequent recalibration. Factory-adjusted pH, pCl, and other px-meters with integrated sensors, usually in combination, have already worked well under difficult conditions, e.g. in maintenance of sewage detoxification plants, field measurements, and in new fields of application for electronic pH measurement.

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For some time, expertly executed electronic (electrometric) pH measurements have been more accurate and less susceptible to falsification by environmental conditions than colorimetric pH determinations using indicator methods. Measurements are now electronic, employing an electrochemical measuring cell, the pH electrode, and the result is defined as $pH = -\log[H^+]$ or in general for px sensors, $px = -\log[X^{\pm}]$, where $[X^{\pm}]$ is found as the activity $a_{X^{\pm}}$, and X^- stands for Cl^-, and X^+ for H^+ ions.

In order to obtain precise or reasonably precise measurements in electrometric determinations of ion activities with known direct-reading devices, the device must be calibrated before each measurement with the aid of standard solutions (calibrating buffer) and frequently recalibrated in prolonged series of measurements. In such measuring devices, e.g. a pH meter, it is required that the asymmetry potential of the measuring chain and the discrepancy between the actual and theoretical measuring-chain slopes be correctable, for which purpose the electrical zero point of the device, a countervoltage taken from e.g. the amplifier, and the amplification factor are customarily made variable. Therefore, the measuring devices usually contain variable voltage dividers, controlled e.g. by manual knobs. The shifting of the electrical zero point and the allowance for temperature influences are often automatic, e.g. through an electronic control, containing a temperature-dependent resistance or a thermistor in the case of temperature corrections. Therefore, known devices always have a corresponding number of controls, which must be operated in a specific manner in calibrating and adjusting with the aid of standard solutions. Frequently, a selector switch is also required for the regulation of various functions. Because of these measures, measuring e.g. pH becomes arduous and time-consuming. Faulty measurements and faulty interpretations

due to adjustment and reading errors, imprecise standard solutions, and erroneous setting of the controls occur frequently. Although attempts have been made to simplify the operation of the devices, such as by using a programmed punched card for setting the variable voltage dividers and (or) by means of diagrammed reading scales under the dials to allow for various measuring temperatures, no substantial progress has been made, and using e.g. the pH meters cannot be made much easier as long as the requirements listed above are considered vital.

Technical Simplification

Advances in px-measurement engineering have brought about substantial technical simplification and thereby the construction in the factory of pH meters adjusted to precision pH buffer solutions in accordance with DIN/NBS standards, using a permanent activating solution developed for practice [1] for the reference electrode and for the glass electrode. Naturally, it is also applicable to other px-meters and display devices with new kinds of maintenance solutions based on a similar principle [2]. For portable measurements, the px-electrodes are integrated into the device, or installed in a suitable flow-through cell for continuous industrial measurements.

The new solution is achieved by, among other things, a fixed setting of the measuring amplifier to factory-adjusted positions and by a suitable choice of electrodes and chemical solutions for filling and external maintenance. External activation via the chemical solution preserves the electrical slope and the zero point of the chain. The amplifier is also adjusted to the mean slope found for qualified modern pH electrodes.

We will briefly describe the filling of the reference electrode with the identical solution mentioned above: the function of the reference electrode

semi-elements (type 2 electrodes) is given by, using the example of silver/ /silver chloride/KCl, NH_4Cl, or NaCl, by the solubility product:

$$L = a_{Ag^+} \cdot a_{Cl^-}$$

where L = solubility product and a = ion activity. The chloride-ion activity is held constant by the activating solution which contains chloride:

$$a_{Cl^-} = k,$$

so that $a_{Ag^+} = L/k$ is constant. According to the Nernst equation, the potential is:

$$E = E_{Ag^+} + \frac{RT}{nF} \ln \frac{L}{a_{Cl^-}},$$

where R = universal gas constant, F = Faraday constant, T = temperature, and n = valence.

Calculated for 25°C, the two equations yield:

$$E_{Ag/AgCl} = E_{Ag^+} + 0{,}05916 \log \frac{L}{k}$$

i.e. the potential of the reference electrode is constant because of the high chloride-ion concentration in the activating solution. The solution "D" [1] is simultaneously a pH buffer.

Deriving the solubility product as a function of pH would take several pages; however, it is evident that the pH of the reference electrode charge should be held constant and not left subject to an unknown drift, as previously. Since this eliminates electrical "recalibration" and since the neutral point in the ion product for water is pH = 7.00 only at 24-25°C, it is best, in order to obtain reproducible comparison measurements, to take measurements at

25°C ± several degrees Centigrade depending on measuring accuracy, and thus to fix the pH meter to this ideal temperature in the factory. For the tropics or medicine and biology fixed at 37°C or e.g. for prolonged field measurements at a mean temperature of 15°C, to this temperature [sic]. With this design and with the chemical solution continuously maintained, there are no longer any controls on the devices, resulting in single-button operation: a power or battery switch. Portable, self-powered devices in this design are shown in Figs. 1 and 2.

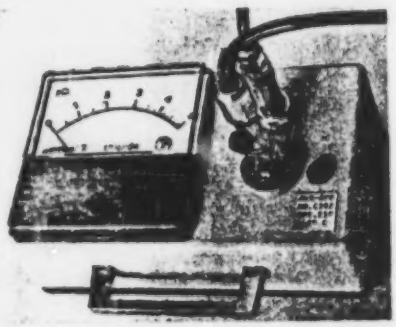

Fig. 1. Chloride meter with direct indication of pCl values ready for immediate use. The same design with pCN electrode serves as trend meter for detoxification of galvanic effluents after cyanide oxidation.

High-Speed Measurement with Electronic Precision

When switched on, the device displays the Test Value of solution D (pH meter) or the solution Cl (pCl meter) [1]. This involves an overall test of all electrometric and electronic functions of the measuring apparatus, e.g. including the px-electrode slope mV/pH, the electrical chain zero point mV (symmetrization), the response time in sec (electrode state), the linearity of the electrode, and the overall function of the device as well as satisfactory battery function. Solution D gives the pH as indicated in Table 1.

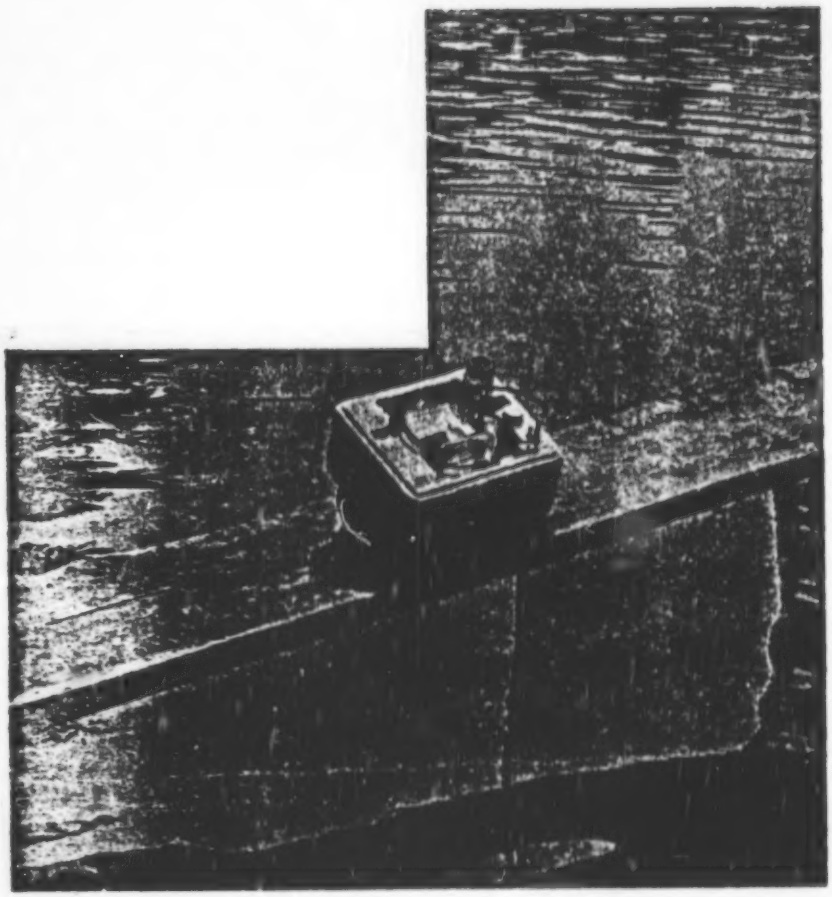

Fig. 2. Manufacturer-adjusted high-speed pH meter for immediate measuring without electrical controls.

Table 1

pH of solution D

15 °C	25 °C	35 °C	
pH=4,03	4,00	4,04	±0,01 pH
a. bei einer Werkjustierung auf 25 °C			
pH=4,73	4,00	4,06	±0,03 pH

Key: a. when adjusted at the factory to 25°C

[Note: Commas in numerals are equivalent to decimal points.]

The chemical solution largely eliminates contamination, e.g. "calcification", and mold or algae attacks are prevented.

The Same Chemical Solution on the "Inside" and "Outside"

Since, on this principle, the charge for the reference electrode is identical with the storage solution for the entire pH measuring chain, the locking cap on the reference electrode can be left unperforated in opposition to previous instructions. The measuring time is limited to 5 min. Overpressure measurements can also be made with the water column up to 12 m, e.g. to obtain a rapid measurement for a body of water, as long as the maximum residence time of 5 min is adhered to. For longer measuring time, a pressure-equalization vessel containing solution (1) is hooked up. If the solution is erroneously diluted with measuring medium, fresh solution is poured in.

Without the previous perforation, the electrode is less contaminated in practice and exhibits the proven, sturdy functions for a great variety of chemical media. The diaphragm based on sintered aluminum oxide is impervious to acid and base, and largely swell-resistant. No organic or contamination-sensitive single crystals are employed in this px-measurement. For pH measurements, it is proven alkali-resistant shatter-proof glass with low electrical resistance. For pCl measurements, pure silver with halogenation in the factory, stabilized by the acidic chemical solution "Cl" with specific pH and pCl values.

pCl Applicable in Practice

The factory-adjusted chloride meter built on the same principle, driven by a dry battery and with a direct pCl scale (pCl meter), can also be constructed as a pH meter. Several examples of interpretation are given. A pCl

value of 1.0 means effectively (as in pH measurements) the activity apCl, i.e. 4450 mg Cl^-/ℓ (after activity conversions) pCl = 3.0 corresponds to about 35.5 mg Cl^-/ℓ and pCl = 5.0 to 0.36 mg Cl^-/ℓ. The pCl measurements can likewise be carried out directly with these chloride meters, with good control by means of the maintenance and test solution "Cl", the pCl of which is 2.0. Environmental media, foods, bodily fluids, and liquids in organs can be monitored rapidly and more frequently with such pCl meters. If one does not wish just to carry out comparison measurements, and wants to avoid activity falsifications, one has the option of measuring directly (pCl scale 0-5) or diluting 1:9 below pCl = 1 and subtracting 1.0 to obtain the pCl of the medium. A conversion table in meq, mg/ℓ, etc. is very useful.

Contamination by seawater, salting of the environment, and medical diagnoses can be made more rapidly or become practical for the first time directly at the site and in sufficient analytical quantity with such devices. The indirect inferences with respect to other types of contamination based on pH and pCl measurements are not insignificant either, because of related equilibria. Parallel conclusions can be drawn from single measurements, as long as the mean values, the extremes, or the optimum ranges for pH or pCl are known. For this purpose, and for wider dissemination of the information on typical pH optima and pH conditions, a handbook is being published on pH and pCl values and other data for wide ranges of applications with introductions to the various special fields and possible interpretations [3].

Continuous Industrial px-Measurement (Final pH Control)

As far as the continuous measurements mentioned at the outset, industrial px-measuring systems based on this design can be manufactured with

factory-calibrated components for immediate use without having to bring in an instrument specialist. The chemical activation of the px-sensor stabilizes the latter in such a fashion that even the diffusion at the diaphragm of the reference electrode and the exchange reactions become better defined. To limit the scope of the work, a discussion of cases with various media occurring in practice and the resulting reactions at the diaphragm are given for the case of pH measurement on high-purity water:

High-purity water with 0.1-10 $\mu\Omega^{-1}cm^{-1}$ or chemically pure water (limited contents of SiO_2, CO_2, etc.) is drawn by the diaphragm of the reference electrode in such a fashion that the diffusion begins to fluctuate widely. A varying water flow velocity simulates different pH values for the medium. The acidic electrode charge with slow outflow via the diaphragm of the reference electrode stabilizes this phenomenon to a certain degree. By combination with a new type of flow guide in the flow-through measuring cell, the effects on the pH electrode are largely restricted to the specific selectivity with respect to pH. The pH and pCl are therefore of increasing importance in high-purity water, since they can be measured simply and reliably, and since these quantities indicate increasing contamination with e.g. silicon dioxide and other components (which affect pH or pCl) and change even before any change in conductivity. Simple measurements with portable devices as in Figs. 1 and 2 are very useful in practice. Of course, prolonged reliability can be achieved only by continuous measurements with recording and perhaps built-in alarm systems.

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